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FINAL REPORT

Photochemically Produced Free-Radicals in Solution

Prepared for the
U.S. Army Research Office (Durham)
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by

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This final report summarizes research studies on photochemically produced free-radicals in aqueous solution carried out in the Department of Chemistry of the University of California, Davis, during the period July 1, 1958 - September 31, 1962. The program was initiated under sponsorship of the Department of the Army - Ordnance Corps under Contract No. DA-04-200-ORD-171, Task Order No. 13. Beginning July 1, 1961, sponsorship was assumed by the U. S. Army Research Office (Durham) under Grant No. DA-ARO(7)-31-124-G42, Project No. 2094-C. The expiration date of the Grant was September 31, 1962.

The research performed under the above sponsorship has either been already published in scientific journals or is currently in press. Full details are, therefore, available in these publications.

STATEMENT OF THE PROBLEM

The object of this work was to develop methods generally applicable to the quantitative determination of free radical formation for photochemical reactions in aqueous solution. The mechanism of the primary step following the absorption of light by molecules in solution is of fundamental importance. For many molecules evidence for free radical formation is inconclusive. Where such evidence is available, more quantitative study is needed.

Free radicals may be determined by free radical traps. The use of olefinic compounds which can act as scavengers by undergoing free radical addition has wide application in the study of mechanisms of thermal and photochemical reactions. For photochemical reactions in water solution, the choice of an appropriate trap is severely limited by considerations of transparency and solubility. As most water soluble olefinic compounds are conjugated double bond system molecules, often involving strong light absorbing structural groups as well, they are generally strong light absorbers in the usual photochemical region and, hence, unsuitable. (See Reference 1).

RESULTS AND CONCLUSIONS

Allyl Alcohol as Scavenger

Allyl alcohol, water soluble and transparent at 2500 Å, proved to be a successful scavenger for free radicals formed in photolysis in aqueous solution. It was used in studies of a number of different systems. Summaries of these studies are hereby given.

Hydrogen Peroxide

The photochemical decomposition of hydrogen peroxide at 2537 Å, has been studied in aqueous solutions with and without added allyl alcohol. At high intensities and low peroxide concentration, the quantum yield for hydrogen peroxide decomposition was independent of intensity and concentration and was found to be 0.94 ± 0.06 in the absence of allyl alcohol and 0.54 ± 0.05 in the presence of allyl alcohol at 27°. These results are consistent with a kinetic interpretation in which the limiting quantum yield in the absence of allyl alcohol should be twice the quantum yield of the primary decomposition of hydrogen peroxide into OH radicals and the limiting yield in the presence of allyl alcohol should be just equal to the quantum yield of the primary decomposition. Evidence for the formation of tetrahydroxyhexene was obtained. This is expected if the mechanism is the addition of hydroxyl radical to allyl alcohol and then association of the diol free-radicals. (See References 2 and 9).

Acetone

The photochemical decomposition of acetone at 2537 Å. has been studied in aqueous solutions with and without added allyl alcohol in the temperature range from 2 to 73°. The quantum yields of the gaseous products, methane, ethane and carbon monoxide, were determined. The results are consistent with a free radical mechanism in which methane is formed both by abstraction of hydrogen atoms from acetone by methyl radicals and by disproportionation between methyl and acetyl radicals. The temperature dependence of diffusion of methyl radicals was considered and shown to be important in the calculation of activation energy differences for abstraction and combination. (See References 3 and 10).

Acetaldehyde

The photochemical decomposition of acetaldehyde at 2537 Å. has been studied in aqueous solutions with and without added allyl alcohol in the temperature range from 27 to 73°. The quantum yields of the gaseous products, methane, ethane, carbon monoxide and hydrogen, were determined. The results are consistent with a combination of a free-radical inter-molecular reaction and an intramolecular reaction which may be a "geminate" free-radical process. (See Reference 4).

Microphotochemistry

The previous studies were conducted using conventional techniques. To take full advantage of newer methods of analysis, flame ionization chromatography detectors, we have developed a method of solution microphotochemistry which has proven to be much more rapid than conventional methods, to be easier to use, and to give results which are equally satisfactory and reproducible.

For use with this method we have developed a method of uranyl oxalate actinometry based on carbon monoxide formed rather than oxalate decomposed. The quantities of carbon monoxide formed were too small for analysis by any existing technique, but it was found that analysis could be accomplished by catalytic hydrogenation of carbon monoxide to methane, which can be determined by flame ionization detectors. The methods have been applied in a study of the photolysis of propionaldehyde in aqueous solution. (See References 5 and 8).

PUBLICATIONS

Journal Articles

- (1) D. H. Volman, J. C. Chen and L. W. Swanson, An Olefinic Free-Radical Scavenger for Photochemical Studies in Aqueous Solutions: Application to the Photolysis of Hydrogen Peroxide and Acetone at 2537 Å. J. Am. Chem. Soc. 81, 756 (1959).
- (2) D. H. Volman and J. C. Chen, The Photochemical Decomposition of Hydrogen Peroxide in Aqueous Solutions of Allyl Alcohol at 2537 Å. J. Am. Chem. Soc. 81, 4141 (1959).
- (3) D. H. Volman and L. W. Swanson, The Photochemical Decomposition of Acetone in Aqueous Solutions of Allyl Alcohol at 2537 Å. J. Am. Chem. Soc., 82, 4141 (1960).
- (4) J. C. Chen and D. H. Volman, The Photochemical Decomposition of Acetaldehyde in Aqueous Solutions of Allyl Alcohol at 2537 Å., J. Am. Chem. Soc. 83, 1047 (1961).
- (5) K. Porter and D. H. Volman, Flame Ionization Detection of Carbon Monoxide for Gas Chromatographic Analysis, Analytical Chem. 34, 748 (1962).
- (6) K. Porter and D. H. Volman, Uranyl Oxalate Actinometer for Microphotochemistry, J. Am. Chem. Soc. 84, 2011 (1962).
- (7) K. Porter and D. H. Volman, Microphotochemistry in Liquid Systems, Photochemistry and Photobiology, In press.
- (8) K. Porter and D. H. Volman, Microphotochemistry in Liquid Systems. The Photolysis of Propionaldehyde, Bull. Soc. Chim. Belg., In press.

Doctoral Dissertations

- (9) C. C. Chen, Photochemistry of Hydrogen Peroxide, University of California, September, 1959.
- (10) L. W. Swanson, The Photochemistry of Acetone in Water, University of California, January, 1960.

SCIENTIFIC PERSONNEL

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